Journal of the Serbian Chemical Society
JSCS-info@shd.org.rs • www.shd.org.rs/JSCS

J. Serb. Chem. Soc. *82* (1) 73–82 (2017)
JSCS–4948

UDC 547.466'581.2'269.3+681.586.74:
628.193:546.492
Original scientific paper

Aminobenzene sulfonic acid-functionalized carbon nanotubes on glassy carbon electrodes for probing traces of mercury(II)

JING LV[1,2], YING TANG[2], LIUMEI TENG[2], DIANYONG TANG[2] and JIN ZHANG[2]*

[1]College of Chemistry and Chemical Engineering, Southwest University, Chongqing 400715, P. R. China and [2]Chongqing Key Laboratory of Environmental Materials & Remediation Technologies, Chongqing University of Arts and Sciences, Chongqing 402160, P. R. China

(Received 19 April, revised 13 August, accepted 3 October 2016)

Abstract: This work reports on a new electrochemical sensing strategy for quantitative monitoring of inorganic mercury(II) in contaminated water by immobilization of poly(*p*-aminobenzene sulfonic acid)-functionalized single-walled carbon nanotubes on a glassy carbon electrode. The electrochemical behavior of the resulting sensor was assessed and optimized. Under optimal conditions, the sensor displayed good electrocatalytic responses to Hg^{2+} reduction ranging from 1.0 μmol L^{-1} to 0.5 mmol L^{-1} with a detection limit of 0.5 μmol L^{-1}. The selectivity against other potentially interfering ions and the applicability in contaminated water samples were also evaluated.

Keywords: electrochemical sensor; *p*-aminobenzene sulfonic acid; single-wall carbon nanotubes (SWCNTs); contaminated water.

INTRODUCTION

Mercury, a well-known global pollutant, is one of the most toxic elements.[1] Typically, its bioavailability, toxicity and bioaccumulation in living organisms are dependent on its chemical form.[2] Inorganic mercury(II) (Hg^{2+}) is one of the most common and stable forms due to its solubility in water. Soluble Hg(II) can accumulate in vital organs through the food chain and cause severe damage to the brain, nervous system, kidneys, heart and endocrine system.[3] Thus, sensitive monitoring of Hg(II) is very important in the analysis of food safety and environmental surveys.

Nowadays, different methods and strategies based on various signal-generation principles have been developed for Hg(II) quantification, such as atomic fluorescence spectrometry,[4,5] atomic absorption spectrometry,[6] inductively coupled plasma-mass spectrometry,[3,7] inductively coupled plasma atomic emis-

---

* Corresponding author. E-mail: zhangjin@cqwu.edu.cn
doi: 10.2298/JSC160419090L

sion spectrometry,[8] high-performance liquid chromatography,[9] ion chromatography,[10] colorimetric detection[11] and sensing strategy. Despite the high sensitivity of conventional methods, they have some limitations, such as high operating costs, inadequate detection limits, or expensive instrumentation. To this end, an alternative strategy that combines the high-efficiency signal-transduction methods with simple and low-cost signal-generation tags would be adventageous.[12] Electrochemical sensors hold great potentials for this purpose because of their high sensitivity, simple and convenient operation, and low cost. The electron transfer between the solution and the underlying electrode not only provides the model for the mechanistic study of electron transport, but also enables the construction of highly sensitive reactors. Therefore, for the development of a high-efficiency electrochemical sensor for the detection of trace Hg(II), the exploration of suitable materials for the fabrication of electrochemical sensors is of great interest. Carbon nanotubes (CNTs) can effectively accelerate some electron-transfer reactions between electrodes and electro-active species, increase the accessible surface area, and enhance electrocatalytic activity. Due to their large specific surface area, excellent electrochemical durability and electrical conductivity, CNTs have gained widespread attention.[13] Carbon nanotubes modified electrodes have been used to detect the biomolecules.[14–16] The surface of single-walled carbon nanotubes (SWCNTs) is comparatively pure due to their great chemical inertness. SWCNTs have good adsorption and electro-catalytic properties after carboxylation. Many researchers have applied SWCNT or functionalized SWCNT to analyze organic compounds and selected metals.[17–19] Moreover, many carbon-based electrodes surface or bulk-modified with SWCNTs have been used for monitoring and analysis, such as carbon paste electrodes[17] and carbon-fiber electrode.[20] Despite their large volume-to-surface ratio and high conductivity, carbon nanotubes alone cannot exhibit good redox characteristics during electrochemical measurements. Inspiringly, recent research was aimed at the development of innovative and powerful functionalized nanomaterials with organic molecules, controlling and tailoring their properties in a very predictable manner to meet the needs of specific applications. The poly(*p*-aminobenzene sulfonic acid) [poly(*p*-ABSA)]-modified electrode has several advantages, such as well-filmed, long stability, little interference, and good electrical conductivity. The detection of organic acids by the poly(*p*-ABSA)-modified electrode was reported.[21,22] To the best of our knowledge, however, there are no reports focusing on poly(*p*-ABSA)-functionalized single-walled carbon nanotubes for electrochemical detection of Hg(II).

Herein, a simple and feasible electrochemical sensing protocol for the sensitive detection of Hg(II) based on poly(*p*-ABSA)-functionalized SWCNTs is reported. The *p*-ABSA monomer was electrochemically polymerized onto a SWCNTs-modified glassy carbon electrode. The assay was realized based on organic–inorganic hybrid nanostructures toward the catalytic reduction of Hg(II). The aim of the present work was to construct a high-efficiency and cost-effective electrochemical sensor for the quantitative monitoring of Hg(II) in environmental samples.

EXPERIMENTAL

Materials and apparatus

Carboxlylated single-walled carbon nanotubes (SWCNT) were purchased from Boyegaoke New Mater. Technol. Co., Ltd. (Beijing, China). Hg^{2+} standards of different concentrations were prepared by dissolving $HgCl_2$ in distilled water. *N*,*N*-Dimethylformamide (DMF) and anhydrous *p*-aminobenzene sulfonic acid (*p*-ABSA) were procured from Chengdu Cdkelong Chem. Re. Co., Ltd. (Chengdu, China). Different pH phosphate-buffered saline (PBS) solution containing 0.9 % KCl were prepared by mixing 0.1 mol L^{-1} KH_2PO_4 and 0.1 mol L^{-1} Na_2HPO_4. All other chemicals were of analytical grade and used as received. Double-distilled water was used throughout this study.

All electrochemical measurements, including cyclic voltammetry (CV) and anodic stripping voltammetry (ASV), were performed using a CHI 660D electrochemical workstation (Shanghai CH Instruments Co., Ltd., China) with a conventional three-electrode system, including a modified glassy carbon disk electrode (GCE, d = 4 mm) as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a platinum-wire counter electrode. The morphology of the modified electrode was obtained using a FEI Quatan 250 scanning electron microscope (FEI Company, USA). The comparative measurement was performed using a Purkinje T9 UV–Vis spectrophotometer (Purkinje General Instrument Co., Ltd., China)

Fabrication of the Hg^{2+} electrochemical sensor

Prior to the experiment, 1.0 mg of SWCNTs was dispersed into 1.0 mL DMF by for 20 min to obtain a homogenous SWCNT suspension. A glassy carbon electrode was carefully polished initially with 0.3 μm and 0.05 μm aluminum oxide, then rinsed in acetone, absolute ethanol and water with sonication for 5 min to obtain a mirror-like surface, and then dried at room temperature. Then 4 μL of the above-prepared SWCNT suspension was cast onto the cleaned GCE using a microsyringe and dried under an infrared lamp (the resulting electrode is denoted as SWCNT/GCE). After gentle washing with distilled water, *p*-ABSA was electrochemically polymerized onto the SWCNT/GCE in pH 7.0 PBS containing 2.0 mmol L^{-1} *p*-ABSA. Polymer growth was achieved within an applied potential ranging from between −1.5 and 1.5 V at 100 mV s^{-1}, and continuously scanning for 10 cycles. After washing with distilled water, the sensor (the resulting electrode is denoted poly(*p*-ABSA)–SWCNT/GCE) was used for the detection of Hg^{2+}. For comparison, a poly(*p*-ABSA)-modified GCE (the resulting electrode is denoted poly(*p*-ABSA)–GCE) was prepared using the same electropolymerization procedure.

Electrochemical measurement for target Hg^{2+}

Before the determination, the poly(*p*-ABSA)–SWCNT/GCE was subjected to scanning cyclic voltammetry until a steady-state cyclic voltammogram was obtained in pH 4.0 PBS. Afterwards, Hg^{2+} standards with different concentrations were added into pH 4.0 PBS. Meanwhile, the electrochemical signal was monitored and recorded based on anodic stripping voltammetry by accumulating Hg^{2+} at –1.0 V for 5 min. The peak current (I_p) was evaluated relative to the baseline.

RESULTS AND DISCUSSION

Electropolymerization of p-ABSA on the SWCNT/GCE

The cyclic voltammograms of the polymerization on the SWCNT-modified GCE are shown in Fig. 1A. The SWCNTs possessed many carboxyl groups, and *p*-ABSA could easily combine to SWCNTs by hydrogen bonds.[23] As seen from the voltammograms, two pairs of redox peaks (peaks a and c and peaks b and d) were observed. During the first scanning run, the *p*-ABSA initially lost an electron, and then a one-electron oxidation of the amino group turns it into its corresponding cation radical, thus resulting in the formation of the anodic peak at 0.25 V (peak a). In addition, the corresponding cathodic peak was observed at –0.1 V (peak c) on the reverse scan, indicating that the cation radical lost a hydrogen ion and generated the *p*-ABSA radical. Thereafter, the radical dimerizes to form 4,4′-disulfohydrazobenzene. With continuous scanning, a cathodic peak at –0.4 V (peak d) was obtained. The reason was attributed to the fact that 4,4′-disulfoazobenzene lost two hydrogen ions and continued to loose two electrons to produce 4,4′-disulfoazobenzene dimers,[24] thus causing another anodic peak at 0.9 V (peak b). Moreover, according to Fig. 1A, the peak currents increased with successive potential scans, indicating that deposition of *p*-ABSA on the SWCNT/ /GCE occurred. Furthermore, the SEM technique was used to investigate the morphologies of modified electrodes (Fig. 1B). Indeed, the SWCNTs layers formed on GCE were randomly distributed along the electrode and a thin film of poly(*p*-ABSA) could be seen on the SWCNTs layers.

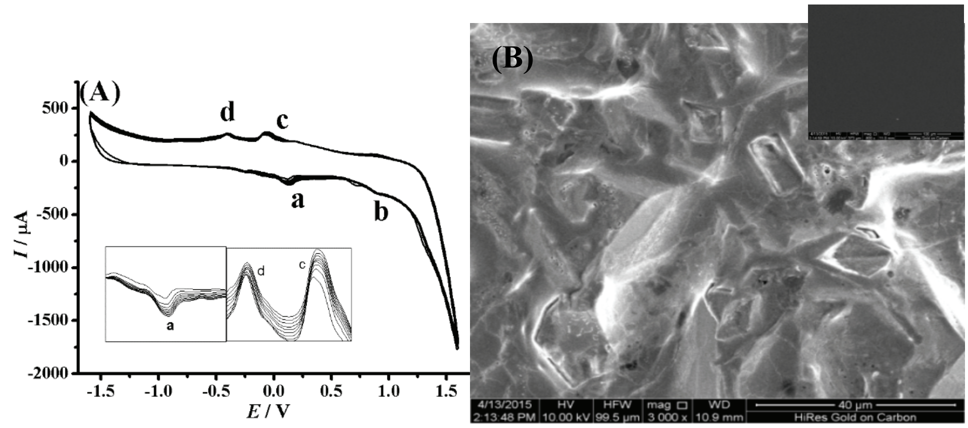

Fig. 1. A) Cyclic voltammograms of *p*-ABSA on SWCNT/GCE during the electropolymerization in pH 7.0 PBS containing 2.0 mmol L^{-1} *p*-ABSA at 100 mV s^{-1} (insets: the corresponding voltammometric curves), B) SEM image of poly(*p*-ABSA)–SWCNT/GCE (inset: SEM image of clean bare GCE).

Electrochemical behavior of mercury(II) on differently modified electrodes

To investigate the amplification efficiency of the as-prepared poly(*p*-ABSA)–SWCNT/GCE, a comparative study using different working electrodes (GCE, poly(*p*-ABSA)–GCE, SWCNT/GCE and poly(*p*-ABSA)–SWCNT/GCE) was performed for the detection of 10 μmol L^{-1} Hg^{2+} in pH 4.0 PBS by ASV. Curve a in Fig. 2 is the baseline. As seen from curve b in Fig. 2, no obvious peak current could be observed at the bare GCE. In contrast, both poly(*p*-ABSA)–GCE (curve c) and the SWCNT-modified GCE (curve d) could increase the voltammometric response toward Hg^{2+}. However, the peak potentials at two modified electrodes were different. This could be attributed to the fact that because of its two groups (amino and sulfo groups) in a counterpoint, strong steric and electron effects prevented the *p*-ABSA from completely forming long end to end chains, which limited the long-distance transfer of electrons. However, the unique structure of SWCNTs determined the properties, *i.e.*, the high surface areas, strong electrical conductivity and adsorption could improve the electrochemical response of the mercury ions. More significantly, when poly(*p*-ABSA) and SWCNT were simultaneously modified onto the GCE, the ASV peak current greatly increased (curve e). Relative to poly(*p*-ABSA)–GCE and SWCNT/GCE, the use of poly(p-ABSA)–SWCNT/GCE could increase the peak current by about 250 and 200 % , respectively. The sidewalls of SWCNTs, having many delocalized π electron systems, can form π–π stack with *p*-ABSA dimers by π–π interaction. Meanwhile, the carboxyl groups of SWCNTs and the amino groups of *p*-ABSA can form a conjugated system, which could accelerate electron transfer.

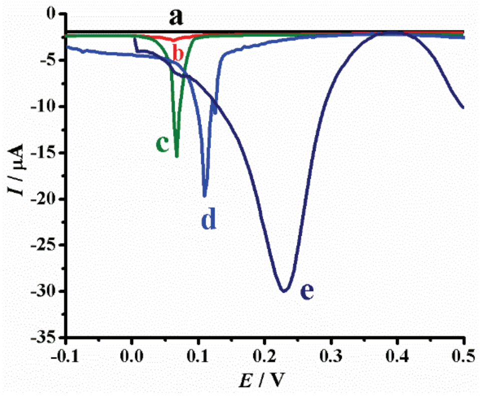

Fig. 2. ASV curves at (a) baseline, (b) GCE, (c) poly(*p*-ABSA)–GCE, (d) SWCNT/GCE and (e) poly(*p*-ABSA)–SWCNT/GCE in pH 4.0 PBS containing 10 μmol L^{-1} Hg^{2+}.

Optimization of experimental conditions

The following conditions (pH, stripping potential, stripping time, amount of SWCNT, and number of polymerization cycles of *p*-ABSA) were optimized to obtain an optimal analytical performance. The effect of the pH of the buffer solution on the electrochemical signal of the Hg^{2+} sensor using 10 μmol L^{-1} Hg^{2+} as an example is shown in Fig. 3A. The results indicated that the current initially increased with the increasing pH from 3.0 to 4.0, and then decreased. The optimal current was obtained at pH 4.0. Therefore, PBS of pH 4.0 was selected as the optimum supporting electrolyte for the detection of Hg^{2+}.

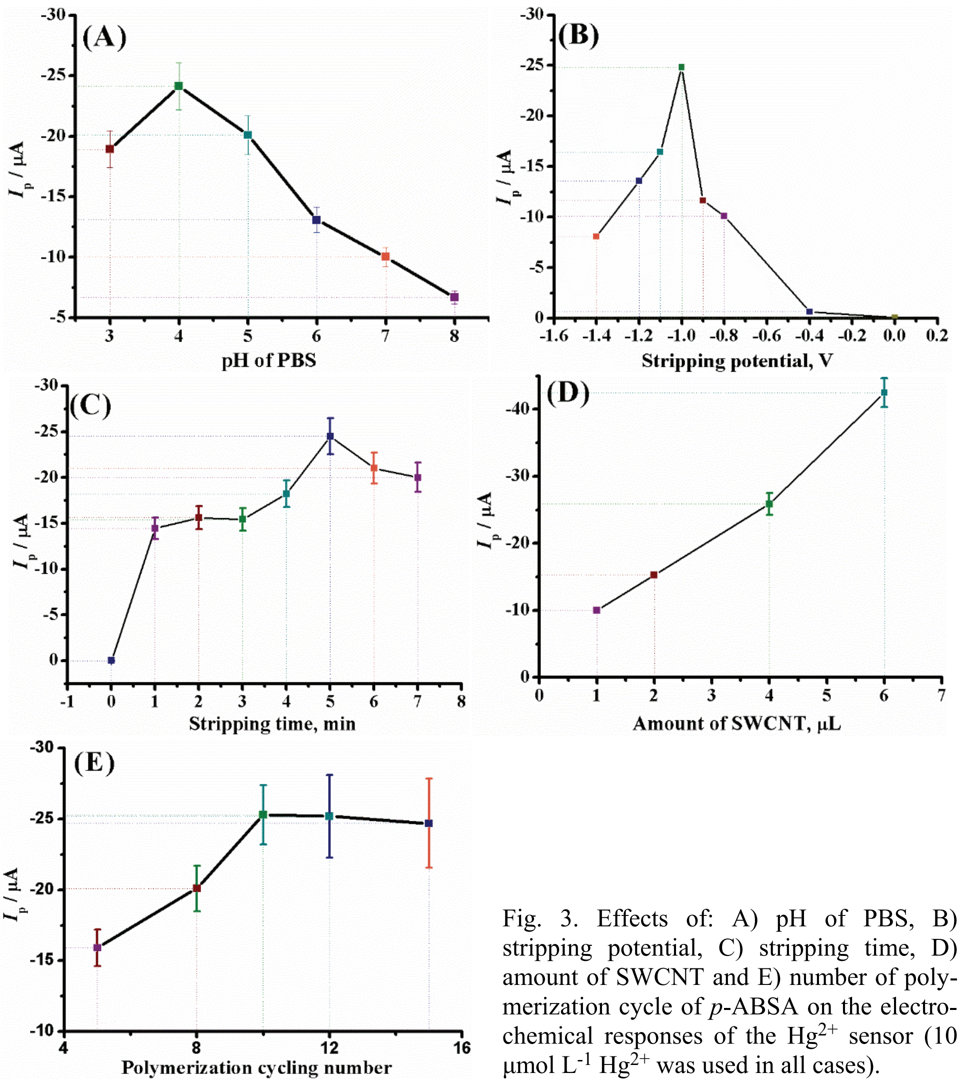

Fig. 3. Effects of: A) pH of PBS, B) stripping potential, C) stripping time, D) amount of SWCNT and E) number of polymerization cycle of *p*-ABSA on the electrochemical responses of the Hg^{2+} sensor (10 μmol L^{-1} Hg^{2+} was used in all cases).

The dependence of the stripping peak current on the stripping potential was examined over the range from 0 to –1.4 V. As shown in Fig. 3B, the current increased rapidly when the potential became more negative. However, the optimal current was obtained at the potential of –1.0 V. Thus, a stripping potential of –1.0 V was selected in this work. At this stripping potential, the effect of the stripping time on the peak current was investigated (Fig. 3C). A maximum peak current was achieved at the deposition time of 5 min; therefore, this time was selected for the preparation of the sensor.

The dosage of SWCNT for the preparation of Hg^{2+} sensor could prominently influence the stripping current. As shown in Fig. 3D, the peak currents increased with increasing SWCNT dosage. However, when the dosage of the SWCNTs suspension was greater than 4 μL, the peak potential shifted. The small surface area of the electrode gave rise to the instability of operation and was counterproductive. Thus, 4 μL dosage of the SWCNTs suspension was used in the preparation of modified electrode.

In addition, we have also monitored the effect of polymerization cycle number of *p*-ABSA on the electrochemical response of the as-prepared sensor. As seen from Fig. 3E, the maximum current was achieved after 10 cycles.

Interference

To investigate the selectivity of the as-prepared poly(*p*-ABSA)–SWCNT/ /GCE, the system was challenged against other metal ions, *i.e.*., Na^+, K^+, Mg^{2+}, Ca^{2+}, Al^{3+}, Cd^{2+}, Ni^{2+}, $Mn^{2+}$and Pb^{2+}. Possible interference with the stripping peak currents of 10 μmol L^{-1} Hg^{2+} was investigated by the addition of the possible interfering ions (100 μmol L^{-1}) to a solution containing 10 μmol L^{-1} Hg^{2+} under the optimized conditions. According to the results (Fig. 4), no interference was caused by the investigated metal ions (signal change below 5 %); hence, the proposed method offers a very high selectivity.

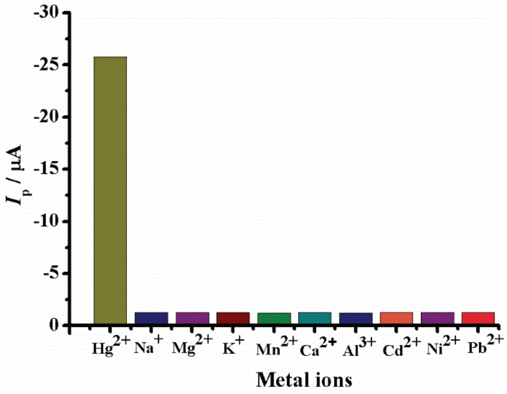

Fig. 4. Effects of possible interfering ions (100 μmol L^{-1}) to a solution containing 10 μmol L^{-1} Hg^{2+}.

*Dose response of poly(*p*-ABSA)–SWCNT/GCE toward the target Hg^{2+} ions*

Under the optimal conditions, different concentrations of Hg^{2+} were determined by the poly(*p*-ABSA)–SWCNT/GCE with ASV measurement in pH 4.0 PBS. The peak current linearly increased with increasing Hg^{2+} concentration in the range of 1.0 μmol L^{-1} to 0.5 mmol L^{-1} (Fig. 5). The detection limit was found to be 0.5 μmol L^{-1}. The correlation coefficient was 0.9939, and the linear regression equation was:

$$I_p / \mu A = -0.0534 c_{Hg^{2+}} / \mu mol\ L^{-1} - 25.220 \qquad (1)$$

The reason for the relatively large intercept in the regression equation mainly arose from the electro-active poly(*p*-ABSA)–SWCNT immobilized on the GCE.

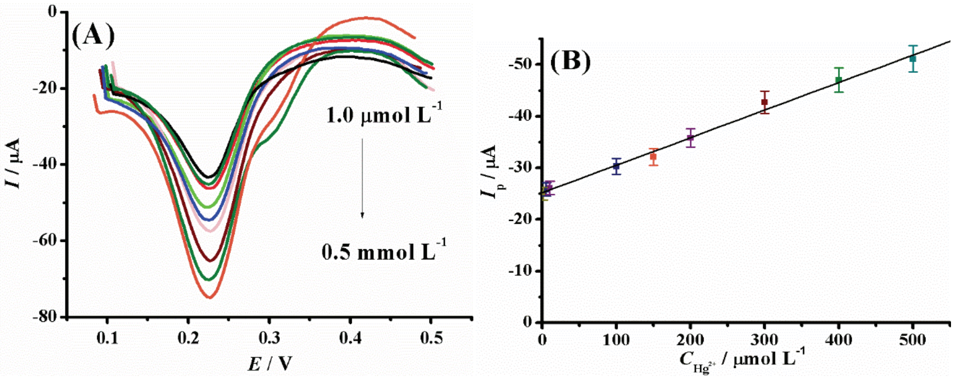

Fig 5. A) ASV responses of the poly(*p*-ABSA)–SWCNT/GCE toward different concentration Hg^{2+} in pH 4.0 PBS (from top to bottom): 1.0, 5.0 and 10.0 μmol L^{-1}; 0.1, 0.15, 0.2, 0.3, 0.4 and 0.5 mmol L^{-1}, and B) the corresponding calibration curve.

Reproducibility and stability

The reproducibility and stability of the poly(*p*-ABSA)–SWCNT/GCE were evaluated under the optimal conditions. The obtained results indicated that the relative standard deviation (*RSD*) of using the same sensor for the determination of 10 μmol L^{-1} Hg^{2+} was 2.3 % ($n = 8$), while that of using the different sensors was 3.9 % ($n = 5$). The stability of the sensor was also studied after storage of several days. The results revealed that the ASV peak currents decreased by 0.9, 1.6, 5.8 and 7.1 % after 4, 7, 10 and 20 days, respectively. Thus, the reproducibility and stability of the sensor were acceptable.

Analysis of real samples

With great reproducibility and stability in buffer, the mercuric sensor was further tested for the determination of Hg^{2+} in spiked water. The obtained results were compared with those of colorimetry using dithizone and a UV–Vis spectrophotometer. The method was performed according to the National Standards of the People's Republic of China (GB5750-85), which is of high accuracy. The comparative results are presented in Table I. Each sample was determined 3 times. The detection results of the two methods were basically the same. The *RSD*s were 1.1–5.8 %, verifying the practical applicability of the method.

TABLE I. Comparison of the obtained results for the determination of Hg^{2+} in spiked water between the poly(*p*-ABSA)–SWCNT/GCE sensor and the UV-Vis-based method

Sample No.	Added Hg^{2+}, μmol L^{-1}	$c_{Hg^{2+}}$ / μmol L^{-1} detected by the sensor	$c_{Hg^{2+}}$ / μmol L^{-1} detected by UV	*RSD* / %
1	17.50	17.65±0.10	17.71±0.23	2.8
2	17.00	17.13±0.07	17.06±0.16	5.5
3	17.50	17.58±0.19	17.61±0.14	1.1

CONCLUSIONS

The electrochemical behavior of Hg(II) on the surface of the chemically modified electrode was studied by ASV. The new electrochemical sensor revealed excellent electrocatalytic activity through the prominent enhancement of the signal current of Hg(II). The results showed that the presence of the SWCNTs and poly(*p*-ABSA) on the glassy carbon electrode could significantly improve the electrical conductivity. In addition, the electrochemical sensor was suited to sensitive voltammometric detection of Hg(II) in the presence of other metal ions. Furthermore, the prepared sensor has good stability and reproducibility. The modified electrode was used in real samples. Hence, a new electrochemical method was developed for the sensitive determination of Hg(II). The designed method was precise, rapid and simple to perform. It is of good utility for further sensor development.

Acknowledgements. This work was supported by the Chongqing Science & Technology Commission, China (Grant No. cstc2015jcyjBX0126) and Key Laboratory of Analysis & Detection for Food Safety (Fuzhou University), Ministry of Education (Grant No.FS-1401).

ИЗВОД

УГЉЕНИЧНЕ НАНОЦЕВИ НА ЕЛЕКТРОДИ ОД СТАКЛАСТОГ УГЉЕНИКА ФУНКЦИОНАЛИЗОВАНЕ АМИНОБЕНЗЕН-СУЛФОНСКОМ КИСЕЛИНОМ ЗА ОДРЕЂИВАЊЕ ТРАГОВА Hg(II) ЈОНА

JING LV[1,2], YING TANG[2], LIUMEI TENG[2], DIANYONG TANG[2] и JIN ZHANG[2]

[1]*College of Chemistry and Chemical Engineering, Southwest University, Chongqing 400715, P. R. China и*
[2]*Chongqing Key Laboratory of Environmental Materials & Remediation Technologies, Chongqing University of Arts and Sciences, Chongqing 402160, P. R. China*

У овом раду је презентована нова стратегија, базирана на сензорима, за електрохемијску квантитативну анализу Hg(II) јона у загађеним водама имобилизацијом једнослојних угљеничних наноцеви функционализованих аминобензен-сулфонском киселином на електроди од стакластог угљеника. Испитано је и оптимизовано електрохемијско понашање добијеног сензора. Под оптималним условима сензор даје добар електрокаталитички одговор на редукцију Hg(II) јона у опсегу 1,0 μmol L^{-1} до 0,5 mmol L^{-1} са

детекционим лимитом од 0,5 μmol L^{-1}. Евалуирана је такође и селекивност у односу на потенцијално ометајуће јоне, као и примењивост у анализи загађених узорака вода.

(Примљено 19. априла, ревидирано 13. августа, прихваћено 3. октобра 2016)

REFERENCES

1. H. Seiler, A. Sigel, H. Sigel, *Handbook on metals in clinical and analytical chemistry*, CRC Press, Boca Raton, FL, 1994
2. P. Krystek, R. Ritsema, *Appl. Organomet. Chem.* **18** (2004) 640
3. Z. Gu, M. Zhao, Y. Sheng, L. A. Bentolila, Y. Tang, *Anal. Chem.* **83** (2011) 2324
4. K. Leopold, L. Harwardt, M. Schuster, G. Schlemmer, *Talanta* **76** (2008) 382
5. J. Sneddon, *Advances in atomic spectroscopy*, Elsevier Science, Amsterdam, 2002
6. D. P. Torres, V. L. Frescura, A. J. Curtius, *Microchem. J.* **93** (2009) 206
7. M. Wang, W. Feng, J. Shi, F. Zhang, B. Wang, M. Zhu, B. Li, Y. Zhao , Z. Chai, *Talanta* **71** (2007) 2034
8. Y. Wu, Y. I. Lee, L. Wu, X. Hou, *Microchem. J.* **103** (2012) 105
9. H. Kodamatani, A. Matsuyama, K. Saito, Y. Kono, R. Kanzaki, T. Tomiyasu, *Anal. Sci.* **28** (2012) 959
10. Q. Liu, *Microchem. J.* **95** (2010) 255
11. X. Xue, F. Wang, X. Liu, *J. Am. Chem. Soc.* **130** (2008) 3244
12. K. S. Guha, R. J. Mascarenhas, T. Thomas, O. J. D'Souza, *Ionics* **20** (2014) 849
13. B. Fang, C. Zhang, W. Zhang, G. Wang, *Electrochim. Acta* **55** (2009) 178
14. Y. Gao, M. Wang, X. Yang, Q. Sun, J. Zhao, *J. Electroanal. Chem.* **735** (2014) 84
15. A. Gaied, N. Jaballah, M. Tounsi, M. Braiek, N. Jaffrezic-Renault, M. Majdoub, *Electroanalysis* **26** (2014) 2747
16. J. Zhu, X. Y. Wu, D. Shan, P. X. Yuan, X. J. Zhang, *Talanta* **130** (2014) 96
17. Z. S. Stojanović, E. Mehmeti, K. Kalcher, V. Guzsvány, D. M. Stanković, *Food Anal. Methods* **9** (2016) 2701
18. L. Meng, J. Jin, G. Yang, T. Lu, H. Zhang, C. Cai, *Anal. Chem.* **81** (2009) 7271
19. G. Liu, Y. Lin, Y. Tu, Z. Ren, *Analyst* **130** (2005) 1098
20. R. Chen, H. Xiao, W. Huang, H. Tong, Z. Wang, J. Cheng, *Chem. Res. Chin. Univ.* **24** (2003) 808
21. H. Tang, G. Z. Hu, S. X. Jiang, X. Liu, *J. Appl. Electrochem.* **39** (2009) 2323
22. L. Zhang, C. Zhang, J. Lian, *Biosensors Bioelectroncs* **24** (2008) 690
23. K. J. Huang, D. F. Luo, W. Z. Xie, Y. S. Yu, *Colloids Surfaces, B* **61** (2008) 176
24. X. Lin, G. Kang, L. Lu, *Bioelectrochemistry* **70** (2007) 235.